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Chromium recharging processes in the $\text{Y}_3\text{Al}_5\text{O}_{12}$: Mg, Cr single crystal under the reducing and oxidizing annealing influence

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ABSTRACT

The influence of reducing and oxidizing annealing on optical absorption spectra of the yttrium aluminium garnet (YAG) single crystal co-doped with Mg and Cr is investigated using step-by-step isothermal and isochronous thermal treatment in H_2 or air flow. The changes in the spectra were analyzed using decomposition on elementary absorption bands of Gaussian shape. The separated absorption bands attributed to the Cr^{4+} ions occupying octahedral and tetrahedral sites in garnet lattice demonstrate different behaviour. The analysis allows to distinguish the electronic recharging process $\text{Cr}^{4+}_{[\text{oct}]} \leftrightarrow \text{Cr}^{3+}_{[\text{oct}]}$ taking place in the octahedral sites of garnet lattice and having lower activation energy from the chromium migration process $\text{Cr}^{4+}_{[\text{tet}]} \leftrightarrow \text{Cr}^{4+}_{[\text{oct}]}$ happening at higher temperatures or longer exposure. Estimations show that approximately 0.2% of total number of chromium ions occupied tetrahedral sites forming phototropic centers in the YAG: Mg, Cr crystal.

Keywords: yttrium aluminium garnet, Cr doping, thermal treatment, phototropic centers, optical characterization, electron paramagnetic resonance.

1. INTRODUCTION

An ability of the tetrahedrally coordinated Cr^{4+} ions to saturable absorption of the Nd-activated lasers' emission is widely used for passive Q-switching.¹⁻⁵ Owing to peculiarities of their luminescent properties these centers are used in tunable lasing in near infrared region as well.⁶⁻⁹ That's why processes of controllable formation of Cr^{4+} centers in tetrahedral sites of laser hosts are of top interest.

The Cr^{4+} centers formation in garnet host crystals is usually forced by simultaneous co-doping with Ca^{2+} or Mg^{2+} ions during the synthesis¹⁰⁻¹¹ that promotes their stabilisation due to the charge compensation. Formation of the Cr^{4+} centers during crystal growth is accompanied by their incorporation into both tetrahedral and octahedral sites of garnet structure while the main part of chromium occupies octahedral sites in three-valence state.¹⁰⁻¹² The dependence of amount of phototropic centers from Ca/Cr ratio was studied in¹⁰. Oxygen vacancies can also contribute to the charge compensation.^{11,12} Healing of anion vacancies by oxygen during post-growth annealing leads to the change of the chromium valence ($\text{Cr}^{3+} \rightarrow \text{Cr}^{4+}$) in crystals¹²⁻¹⁵ and particularly to increase of the phototropic centers concentration. The reducing and oxidation annealing can change the ratio of $\text{Cr}^{4+}/\text{Cr}^{3+}$ but the details of this process was not studied and understood well due to complexity of processes with chromium participation in co-doped garnets. The present work is devoted to further studying peculiarities of the chromium recharging process and phototropic centers formation taking place in the yttrium-aluminium garnet ($\text{Y}_3\text{Al}_5\text{O}_{12}$) co-doped with Mg and Cr subjected to reducing annealing in the H_2 and oxidation annealing in the air flow.

2. EXPERIMENTAL

The yttrium-aluminium garnet single crystals co-doped with Cr and Mg (YAG: Mg, Cr) were investigated. The crystals of high chemical purity have been grown by Czochralski method along [111] direction in the ($\text{N}_2 + 3\% \text{O}_2$) atmosphere with

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growth rate of 2 mm per hour. The samples were prepared in the form of plates with diameter of 10 mm and thickness of 1 mm by crystal cutting perpendicular to growth axis and their surfaces were polished up to optical quality.

The thermal treatment in both reducing and oxidising atmosphere has been performed gradually. The isothermal treatment of as-grown crystal in the hydrogen (H_2) flow at temperature $875^\circ C$ was fulfilled first with net time from 15 min to 8 hours. Then the reduced and as-grown samples were subjected to the isochronous annealing in air during 30 min at each temperature in the sequence at 700, 800, 940, 1020, 1200 and $1400^\circ C$. The annealing in air during 2 hour at $1400^\circ C$ also was performed in the end of an experiment.

Optical absorption spectra of the samples were calculated from transmission spectra, that was measured using "Specord M-40" (Carl Zeiss Jena) and "Lambda-2" (Perkin-Elmer) spectrophotometer in the spectral range $50000 \dots 8000 \text{ cm}^{-1}$ at room temperature. An effect of thermal treatment was analysed using additional absorption (AA) spectra. The last were determined as an excess absorption of the sample under consideration relatively to the totally reduced one excepting the case of oxidising annealing of the as-grown samples when the AA spectrum was determined relative to the initial spectrum of the as-grown sample. Decomposition of the AA spectra of the samples using Gaussian-shaped lines was carried out. It was established that the six Gaussian lines describe satisfactorily the AA spectra in the $40000 \dots 12000 \text{ cm}^{-1}$ range. Absorption band of the $Cr^{4+}_{[tet]}$ ions with maximum at 9400 cm^{-1} in the $13000 \dots 8000 \text{ cm}^{-1}$ range was not taken into account because of its nature was established with enough reliability¹²⁻¹⁷ and it does not overlap another bands in the spectrum. After decomposition of all AA spectra the positions and widths of each line were averaged and fixed. Afterwards amplitudes of elementary absorption bands were determined repeatedly for each AA spectra.

Total concentration of chromium content was determined by the Cr^{3+} optical absorption band intensity in entirely reduced sample as well as by intensity of EPR spectrum. The sample made from the $YAG:Cr^{3+}$ crystal without co-doping of Mg^{2+} was used as a reference sample. The Cr^{3+} concentration in it was determined by chemical analysis. Electron paramagnetic resonance (EPR) measurements were carried out at room temperature using commercial Radiopan SE/X-2543 (Poland) X-band ($\nu \cong 9.4 \text{ GHz}$) spectrometer with 100 kHz magnetic field modulation. The concentration of Cr^{4+} ions in tetrahedral sites of $YAG: Mg, Cr$ samples was estimated by intensity of detached absorption band with maximum at 9400 cm^{-1} in accordance with data presented in¹⁷.

3. RESULTS AND DISCUSSION

Absorption spectrum of the as-grown $YAG: Mg, Cr$ crystal is presented by the curve 1 in Fig. 1a as well as its spectra after reducing (curve 2) and oxidising (curve 3) annealing. The characteristic changes of absorption spectra of $YAG: Mg, Cr$ after reducing and oxidising are well coinciding with those observed in the past.¹³⁻¹⁵ The completely reduced sample got a green colour and its absorption contained two characteristic absorption bands only at 23040 and 16450 cm^{-1} connected with the Cr^{3+} transitions.¹⁸ That's why the additional absorption calculated relatively to spectrum of the completely reduced sample may be interpreted as the absorption of the chromium ions of higher valence.

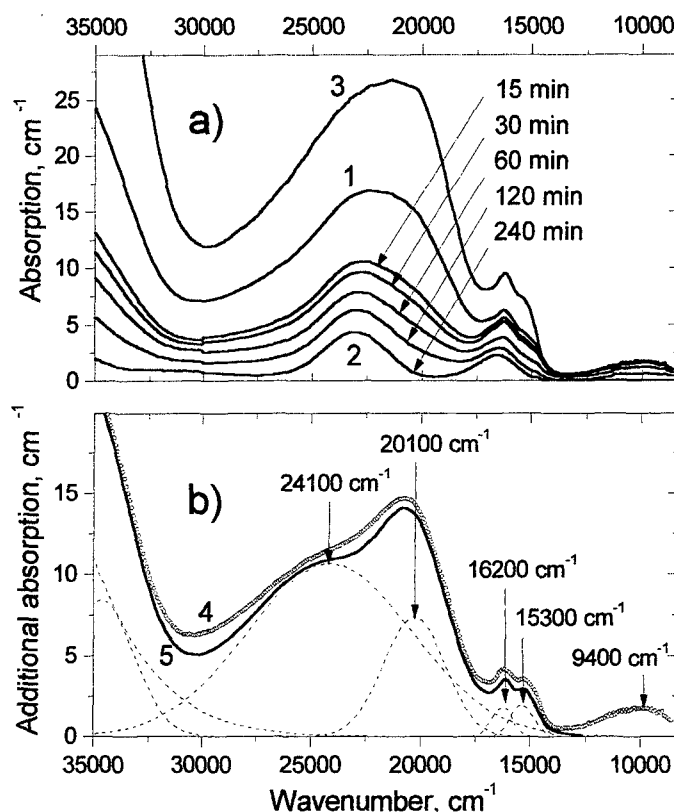
Change of the absorption spectrum during the isothermal reducing annealing in H_2 flow at $875^\circ C$ is also presented in Fig. 1a by the curves marked with arrows and are situated between curves 1 and 2. After four hours of reducing annealing no changes were observed further up to net time of annealing of 8 h. Absorption spectrum of the reduced sample was identical with the spectrum of satellite sample subjected to annealing in hydrogen flow during 10 h at $1200^\circ C$. The last confirms that reducing of the sample occurs practically completely after the 4-hour annealing in H_2 flow at $875^\circ C$. The spectrum changes happen in the opposite direction during the isochronous oxidising annealing in air of the preliminary reduced $YAG: Mg, Cr$ sample. The spectrum of the preliminary reduced sample subjected to the oxidising annealing at $1400^\circ C$ during 2 h occurs practically coinciding with that of the as-grown sample after the same thermal treatment.

An example of the AA spectrum of the as-grown $YAG: Mg, Cr$ crystal relatively to the completely reduced one is shown by the curve 4 in the Fig. 1b as well as its approximation (curve 5) by the sum of Gaussian-shaped absorption bands depicted by dashed lines. It can be seen from the Fig. 1b the set of six elementary bands describes satisfactorily the additional absorption spectrum in the $35000 \dots 13000 \text{ cm}^{-1}$ range. Some of them can be interpreted on the base of a number of published results.^{10,12,15-17} The absorption bands with maxima at 16200 and 15300 cm^{-1} originate from transitions of tetrahedral Cr^{4+} ions^{15,16} as well as absorption in the near-IR region with maximum at 9400 cm^{-1} mentioned above. The absorption lines with maxima at 24100 and 20100 cm^{-1} form the non-elementar broad and intense band in the region $17000 \dots 30000 \text{ cm}^{-1}$ whose nature is under discussion over more than ten years. Various suppositions were published on the base of the energy level scheme calculation as well of non-direct experimental observation. They connected this band with the octahedral Cr^{4+} intracenter transitions^{12,16} as well as with charge transfer transitions with participations of octahedral Cr^{4+} shells¹⁶ and charged oxygen vacancies¹⁵. The last possibility looks as improbable one because as it was shown in^{12,19} the oxygen vacancies exist in co-doped garnet as complexes $[Me^{2+}V_O]$ and are absorbing in UV region. The similar

evidences were found in ²⁰ where the strong absorption band likely connected with such complexes was observed in YAG: Mg, Cr epitaxial layers at 35710 cm⁻¹. That is why we shall consider the Cr⁴⁺ situated in octahedrons as more probably responsible for absorption at 20100 and 24100 cm⁻¹ in accordance to ^{12,16}.

In this connection it should be emphasised that the nature of UV absorption in the region with wavenumbers higher than 30000 cm⁻¹ is also not clear yet and is under discussion in literature. The Cr⁶⁺ ions, charged oxygen vacancies or complexes like [Me²⁺V_O] as well as uncontrollable impurities are considered as responsible for absorption in this region. ^{10,15,19}

Fig. 1. (a) Absorption spectra of the YAG: Mg, Cr crystal registered in as-grown sample (1), after reducing annealing in H₂ flow at 1200°C during 10 h (2) and after annealing in air at 1400°C during 2 h (3) samples (curves between 1 and 2 represent change of absorption spectrum of the YAG: Mg, Cr crystal during isothermal reducing in H₂ flow at 875°C); (b) Additional absorption of the as-grown crystal relative to reduced one: experimental data (4) and their approximation (5) by set of Gaussian lines (elementary lines are represented by dashed lines).



Dependencies of the absorption spectrum components' intensity during isothermal reducing annealing at 875°C is plotted in the Fig. 2 as normalised ones to the initial absorption of each Cr⁴⁺- connected band of as-grown YAG: Mg, Cr crystal.

It is clearly seen that two types of the bands' behaviour can be distinguished: the absorption bands conforming to the octahedral Cr⁴⁺ ions start to decrease immediately from beginning of annealing and is slowly continuing at least four hours. In contrast, the Cr⁴⁺_[tet] absorption bands begin much later (in second half of hour) and practically stop after 2 h of annealing.

It is natural to suggest that the changes happening just after start of annealing are connected with electronic processes of chromium ions recharging while the second stage can be explained by ion migration processes, which require higher energy (the same as temperature) or longer time for their activation. On the first stage the Cr⁴⁺ ions occupying octahedra can easy change their valence to "3+" according to reaction:

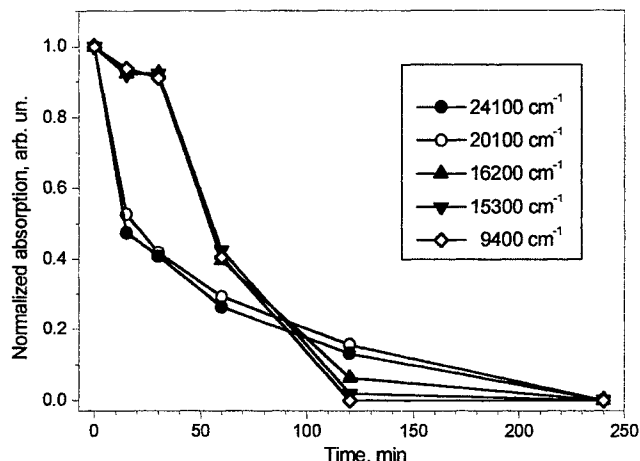


It does not need the ion migration and is caused by loss of oxygen on surface of the crystal that has to be compensated in order to save charge balance. The Cr⁴⁺ reducing process to the Cr³⁺ is impossible in tetrahedra because the Cr³⁺ ions are too big to occupy these sites. ^{12,16} When the ion migration is activated on the second stage the Cr⁴⁺ ions can move from the tetrahedra to octahedra:



where the reaction (1) can take place again.

Fig. 2. Dependence of normalised absorption of separate bands during isothermal reducing annealing of the as-grown YAG: Mg, Cr crystal in H_2 flow at $875^\circ C$.



Different behaviour of two groups of absorption bands is found also during isochronous oxidation annealing of both samples subjected to it – the preliminary reduced crystal and as-grown one. These dependencies are shown in Fig. 3a and 3b, respectively. The AA values presented in Fig. 3b are calculated relatively to the level of the as-grown crystal. In this case the reactions (1) and (2) happen in opposite direction and in opposite order. That's why the increase of the octahedral Cr^{4+} absorption starts just at relatively low temperatures. It is clearly observed in the temperature range below $800^\circ C$ for as-grown crystal and may be, probably, connected with recharging both the equilibrium oxygen vacancies being present in the crystal and the Cr^{3+} ions owing to oxidation reaction on the surface of crystal. The increase of phototropic centres takes place since the migration of chromium is activated by rise of temperature.

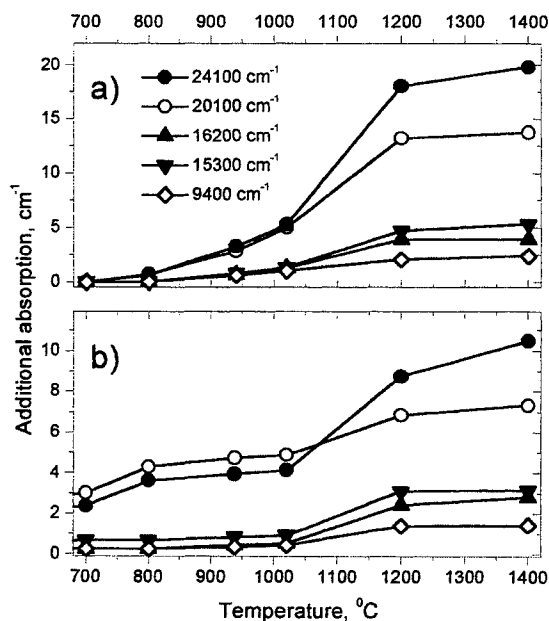
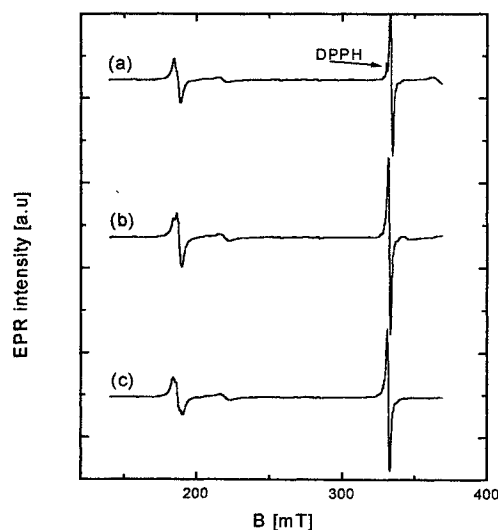


Fig. 3. Dependence of separate absorption bands' intensities during the 30 min isochronous annealing in the air for completely reduced YAG: Mg, Cr (a) and as-grown YAG: Mg, Cr (b) samples.

Fig. 4. EPR spectra of the Cr^{3+} ions in YAG: Mg, Cr single crystal, registered in magnetic field B parallel to the $[111]$ direction; (a) as-grown sample, (b) after annealing in the air at $1400^\circ C$, (c) after annealing in the H_2 atmosphere at $1000^\circ C$.



It may be noted that observed behaviour of separated absorption bands does not contradict to the interpretation of absorption spectrum of co-doped YAG: Mg, Cr given in ¹⁵ because in this case the changes of absorption under reducing

and oxidising annealing can be explained again by electronic recharging and ion migration processes. The first process results in this consideration in recharging of oxygen defects.

EPR spectra of the Cr^{3+} ions in the as-grown crystals as well as annealed ones show that Mg co-doping and annealing at oxygen or hydrogen do not change of the local symmetry and crystal field parameters of the Cr^{3+} impurity centres typical for YAG:Cr^{3+} (Fig. 4). The Cr^{3+} concentrations were determined from intensities of EPR spectra for [111] crystal axis parallel to the magnetic field using DPPH standard ($N = 8 \cdot 10^{15}$ spins). It remains nearly constant within experimental error, independently of the annealing process of the Mg co-doped samples.

The Cr^{4+} concentration in tetrahedral sites was determined from intensity of absorption at $1.06 \mu\text{m}$. Estimations of the Cr^{3+} and Cr^{4+} concentrations in the YAG: Mg, Cr crystal under investigation gave the following values: the concentration of Cr^{3+} in the completely reduced sample was equal to $2 \times 10^{20} \text{ cm}^{-3}$ while the concentration of phototropic $\text{Cr}^{4+}_{[\text{tet}]}$ centres after oxidation annealing became $4 \times 10^{17} \text{ cm}^{-3}$ that corresponds to 0.2 % of total number of the Cr ions. The small amount of Cr^{4+} ions participating in the observed processes does not allow to observe practically any changes in intensity of EPR signals of the Cr^{3+} ions after both reducing and oxidation annealing.

4. CONCLUSIONS

The processes of the chromium impurity centres transformation are investigated using decomposition analysis of absorption spectra of the YAG: Mg, Cr single crystal subjected to reducing and oxidising graduated annealing.

Absorption bands separated by mean of spectrum decomposition clearly demonstrate two different behaviours during after-growth thermal treatment of crystal. The YAG: Mg, Cr absorption changes in the $28000 \dots 17500 \text{ cm}^{-1}$ range are mainly determined by electronic recharging that can be interpreted as reaction $\text{Cr}^{4+}_{[\text{oct}]} \leftrightarrow \text{Cr}^{3+}_{[\text{oct}]}$ taking place in octahedral sites of garnet lattice and having lower activation energy. The chromium migration process $\text{Cr}^{4+}_{[\text{tet}]} \leftrightarrow \text{Cr}^{4+}_{[\text{oct}]}$ happening at higher temperatures or longer exposure is responsible for absorption changes in the $17500 \dots 8000 \text{ cm}^{-1}$ range.

Our estimation show that only about 0.2 % of total number of chromium impurity ions in the crystal under investigation can occupy tetrahedral sites forming phototropic centres and participate in the observed processes. The small amount of this part in comparison with total chromium content does not allow to observe by EPR any remarkable changes in local symmetry, crystal field parameters and microwave absorption intensity of the Cr^{3+} centres in octahedral sites of YAG: Mg, Cr crystal subjected to reducing and oxidising annealing.

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